



TITLE:

Catalytic properties of cold-worked noble metals for the oxidation of carbon monoxide

AUTHOR(S):

Kishimoto, Shozo

CITATION:

Kishimoto, Shozo. Catalytic properties of cold-worked noble metals for the oxidation of carbon monoxide. The Review of Physical Chemistry of Japan 1976, 45(2): 88-92

ISSUE DATE:

1976-02-29

URL:

<http://hdl.handle.net/2433/47019>

RIGHT:

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, Vol. 45, No. 2, 1975

CATALYTIC PROPERTIES OF COLD-WORKED NOBLE METALS FOR THE OXIDATION OF CARBON MONOXIDE

BY SHOZO KISHIMOTO

The oxidation of carbon monoxide was studied on cold-worked metals (Pd, Ag, and Au) to compare the characteristics of the catalytic properties. On palladium, when the reaction was carried out on the freshly prepared catalysts at reaction temperatures below 300°C, the two periods (acceleration and steady state period) were always observed in the course of the reaction. From the observation of the dependence of annealing temperature upon the catalytic activity, it was considered that the acceleration period is the process of the production of new active sites by the reaction itself and that the presence of lattice defects (dislocations) in the crystal plays a role for the reaction to initiate and serves to create the active sites. These facts were almost the same as in the case of platinum catalyst. In the cases of silver and gold, no acceleration period was observed and the annealing had no influence on the catalytic activity. It is suggested that under the conditions of the present experiments the difference in the catalytic properties among these metals is due to the difference in the strength of metal-oxygen bond and in the stability of the active sites.

Introduction

It has been stated by Bond¹⁾ that a particular feature of the oxidation catalysis by molecular oxygen on metals is the rearrangements which metal surfaces suffer during the reaction. These changes seem to induce the considerable changes in the catalytic activity. Despite the intense interest in the oxidation catalysis, there have been a few fundamental studies of the oxidation reaction by metals²⁾. We have recently reported the change in the catalytic activity of cold-worked platinum during the course of the oxidation reaction of carbon monoxide³⁾. When the rate of reaction is plotted against time in the reaction temperature range 250°–325°C, the rate increased gradually with the progress of the reaction and attained a steady limiting value, that is, two periods were observed in the course of the reaction: an acceleration period and a steady state period. Furthermore, it was found that the length of the acceleration period is strongly dependent on both the annealing conditions of the catalyst and the reaction temperature, but the rate in the steady state is independent of the catalyst history. These results indicated that the acceleration period is the process of the

(Received June 30, 1975)

- 1) G. C. Bond, "Catalysis by Metals", p. 447. Academic Press, London and New York (1962)
- 2) H. Leidheiser Jr. and A. T. Gwathmey, *J. Am. Chem. Soc.*, **70**, 1200, (1948); A. T. Gwathmey and R. E. Cunningham, "Advances in Catalysis", Vol. 10, p. 57, Academic Press, New York (1958); R. Y. Meelheim, R. E. Cunningham, K. R. Lawless, S. Azim, R. H. Kean, and A. T. Gwathmey, *Proc. Int. Congr. Catal.*, 2nd, Paris, I, 2005 (1961)
- 3) S. Kishimoto, *Bull. Chem. Soc. Jap.*, **48**, 1937 (1975)

creation of new active sites by the reaction itself and that the presence of dislocations in the crystal plays an important role for the reaction to initiate and serves to create the active sites. It seems probable that a similar situation exists in the cases of other metals. Palladium, silver and gold are also known to be effective for the oxidation of carbon monoxide. The purpose of the present study is to compare the characteristics of the catalytic properties of these metals.

Experimentals

Pure metal wires (99.9% or higher purity) were used as the catalyst. The reaction was carried out in a static system on cold-worked specimens in the form of ribbon (surface area approximately 15 cm^2) over the temperature range from 250° to 400°C . A stoichiometric mixture of CO and O_2 was used for all experiments at an initial pressure of 100 Torr and the product, CO_2 , was continuously condensed by a liquid nitrogen trap connected to the reaction vessel. The main features of the preparation of cold-worked and annealing catalysts, and the preparations of the reacting gases have been described in the preceding paper³). The changes in hardness of the metals on annealing were determined by a micro-vickers hardness tester.

Results and Discussion

The oxidation on Pd occurred at conveniently measurable rates in the reaction temperature range 250° – 300°C . Fig. 1 (A) shows a typical reaction course (first run) at a reaction temperature of 265°C on the catalyst annealed at 350°C for 1 hr in vacuum. Curve (B), the change in the rate with time, is derived from the values in curve (A).

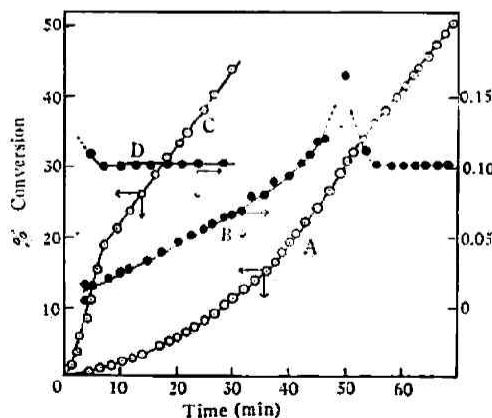


Fig. 1 Oxidation of CO on Pd annealed in vacuum at 350°C (reaction temperature 265°C) (A) and (B), first run: (C) and (D), second run

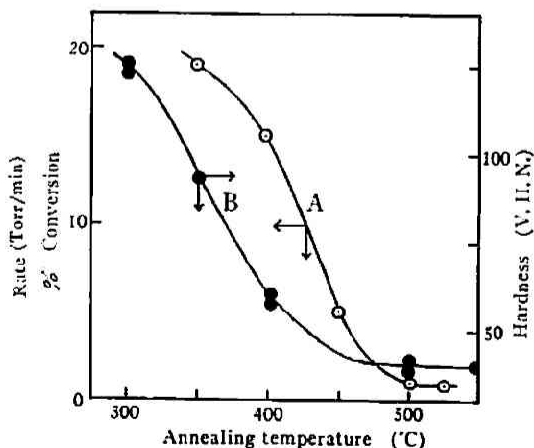


Fig. 2 Dependence of the catalytic activity (A) and hardness (B) on annealing temperature (The activities are expressed as a per cent conversion at a fixed reaction time 40 min at 265°C)

As the reaction proceeds, the rate first increases, passes through a maximum, and then attains to a constant value. Thus, in analogy with the case of Pt, the two periods, an acceleration and a steady state period, can be identified in the reaction course³⁾. Curves (C) and (D) show the results of second run which are obtained with a new dose of the reacting gases after the first run. Such a constant activity remains unaltered in following runs. The acceleration process which is apparently accompanied by the progress of reaction was found to be strongly dependent on the annealing conditions of the catalyst. Fig. 2 (A) shows per cent conversion for the first run on the different specimens annealed in vacuum for 1 hr at various temperatures at a fixed reaction time 40 min. The change is considerable at 350°–500° C. As Fig 2 (B) shows, a change in hardness of this metal takes place in the range 300°–500° C. This change is attributed to the disappearance of dislocations in the crystal produced by cold-working⁴⁾. It has been discussed in the previous papers that the change in the roughness factor of the surface with annealing is not related to the drastic change in the catalytic activity as shown in curve (A)^{4,5)}. On the other hand, the rates at the steady state are nearly the same regardless of the catalyst history at the same reaction temperature. These behaviors are almost the same as for Pt catalyst except for the temperature range occurring the decrease in the activity. It seems to be quite all right to support the conclusion that for the experimental conditions chosen the presence of dislocations in the crystal plays an important role for the initiation of the reaction and for the creation of new active sites in the acceleration process³⁾. It is well known that Pd is not oxidized by O₂ at ordinary temperatures but the formation of a thin oxide layer occurs if this metal is heated in O₂ at temperatures above 300° C⁶⁾. A fresh catalyst annealed at 500° C in vacuum (deactivated catalyst) was pretreated in O₃ for 1 hr at 300° C and followed by reduction in H₂ at 300° C. When the reaction was carried out on this surface, no acceleration period was observed and the reaction course was nearly the same as that activated by exposure to the reacting gases at the reaction temperature. However, this enhanced activity decreased by the subsequent treatment above 500° C in vacuum. It was observed by means of a scanning electron microscope that there is no visible change in the surface structure before and after the oxidation-reduction treatment. On the basis of these data, it seems reasonable to assume that the active sites generated by the reaction have their origin in a kind of surface defects created by the cyclic oxidation-reduction process of the surface involved in the catalytic reaction. On the other hand, as Fig. 1 (B) shows, the activity is not infinitely increased even when such defects are produced. The reason for the presence of maximum in the reaction course may be that as the concentration of defects increases in the acceleration period, stronger interactions among them are expected, and hence the active sites tend to be annealed out at temperatures at which catalysis is in progress. It is suggested that the stability of these active sites varies directly with the temperature required for the diffusion of the atoms on the surface, which the temperature is a function of their melting point.

The reactions on Ag and Au proceeded with observable rates above 350° C. It was found that the pressure of the reactant *vs.* time curves are linear and no acceleration period is observed, in

4) I. Uhara, *et al.*, *J. Phy. Chem.*, **67**, 996 (1963); S. Kishimoto, *ibid.*, **77**, 1719 (1973)

5) I. Yasumori, T. Kabe, and Y. Inoue, *ibid.*, **78**, 583 (1972)

6) E. M. Wise, "Palladium, (Recovery Properties, and Uses)", p. 21, Academic Press, New York and London (1968)

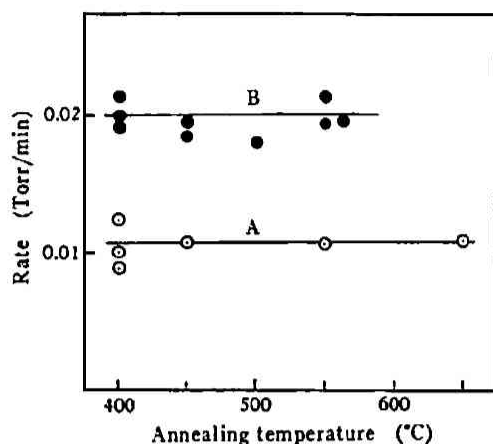


Fig. 3 Dependence of the catalytic activity (rate of reaction) of Au (A) and Ag (B) on annealing temperature (reaction temperature 390 °C)

contrast to the situation with Pt and Pd. Such a constant activity remains unchanged in the subsequent runs. Fig. 3 shows that the annealing above 400 °C has no influence on the catalytic activity of these metals. The previous studies indicated that the recovery temperature ranges (disappearance temperature of dislocations) for Au and Ag used in these experiments are in the range of 100°–200 °C and 70°–250 °C, respectively^{5,7)}. Accordingly, in these cases, dislocations produced by cold-working can not responsible for the active sites, since the catalysts are already annealed at 400 °C before the experiments are made. It is known that the chemisorption of O₂ on Au does not occur readily. Daglish and Eley in studying CO oxidation on Au, suggested that O₂ is only adsorbed on special sites such as dislocations during the oxidation reaction of CO⁸⁾. It has been estimated in fact that the density of dislocations is generally about 10⁶–10⁸/cm² even after the annealing at higher temperatures⁹⁾. In the case of Ag, it is speculated that even if the active sites can be produced by a similar process to the cases of Pt and Pd, these are destroyed rapidly at the temperatures at which the catalysis is being studied.

Correlations between the strength of metal-oxygen bond of oxidation catalysts and their activity have been made for the oxidation of several type molecules⁹⁾. If CO oxidation occurs predominantly on the Eley-Rideal type between chemisorbed O₂ and gas-phase CO, it is accepted that the difference in the catalytic activity between the metals is due to the difference in the strength of the metal-oxygen bond. When the catalytic activities at the stationary state are compared at the reaction temperature of 295 °C, the relative activities of four metals are given by Pd > Pt > Ag > Au. This order may be correlated with data for the heats of formation of metal oxides.

7) S. Kishimoto and M. Nishioka, *J. Phys. Chem.*, **76**, 1907 (1972)

8) A. G. Daglish and D. D. Eley, *Proc. Int. Congr. Catal. 2nd, Paris*, **2**, 1615 (1961)

9) "Recovery and Recrystallization of Metals," Commonwealth Scientific and Industrial Research Organization, Australia (1963)

10) W. R. Patterson and C. Kamball, *J. Catal.*, **2**, 465 (1963); G. K., Borekov, *Discuss. Faraday Soc.*, **41**, 285 (1966); Y. Moro-oka, Y. Morikawa, and A. Ozaki, *J. Catal.*, **7**, 239 (1967)

Acknowledgment

The author wishes to express sincere thanks to Professor Emeritus I. Uhara for helpful discussions.

*Department of Chemistry
Faculty of Science
Kobe University
Rokkodai, Nada-Ku
Kobe 657
Japan*